California Environmental Protection Agency

Air Resources Board

APPENDICES

For Report

Ambient Air Monitoring
for Chlorothalonil in Fresno County – Summer 2002

Prepared by
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Project No. P-02-002

Date: November 3, 2003

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Protocol for the Application and Ambient
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In Fresno County During Summer, 2002

California Environmental Protection Agency

Air Resources Board

Protocol for the Application and Ambient Air Monitoring for Chlorothalonil In Fresno County During Summer, 2002

Quality Management Branch
Monitoring and Laboratory Division

Project No.
P-02-002

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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I. Introduction

At the request (January 2, 2002 Memorandum, Helliker to Lloyd) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide chlorothalonil in Fresno County over a six week ambient monitoring program and over a three day application monitoring program. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The ambient monitoring will be conducted for 6 consecutive weeks between May 26 and July 6, 2002 to coincide with the use of chlorothalonil as a fungicide. California growers primarily use chlorothalonil on tomatoes, potatoes, onion, celery, carrots and garlic.

The sampling and analysis for chlorothalonil will follow the procedures and quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version)(Attachment I) as well as the procedures described in the "Standard Operating Procedure for the Analysis of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (Chlorothalonil) in Ambient Air" (Attachment II) and the pesticide adsorbent tube sampling procedures outlined in Attachments III and IV.

II. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The sampling manifold is shown in Figure 1. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (on dry ice) or in a freezer until desorbed with organic solvent. The tubes are 8 mm x 110 mm with 400 mg XAD-2 in the primary section and 200 mg in the secondary section. The flow rate of 3.0 standard liters per minute (slpm) will be accurately measured and the sampling system operated continuously for 24 hours (ambient) with the exact operating interval recorded in the log book. The tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above roof tops for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, rotameter (or needle valve), train support, and either a 12 volt DC or a 115 volt AC vacuum pump. Tubes are prepared for use by breaking off the sealed glass ends and immediately inserting the tube into the Teflon fitting. The tubes are oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. A needle valve with a range of 0-5 sLpm is used to control sample flow rate. The flow rates will be set using a calibrated digital mass flow meter (MFM), scaled from 0-5 sLpm, before the start of each sampling period. The flow rate is also checked and recorded, using the MFM, at the end of each sampling period. Samplers will be leak checked prior to each sampling period, with the sampling tubes installed. Any change in flow rates will be recorded on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included as Attachment III (ambient) and IV (application).

Ambient Monitoring

The DPR recommendations for chlorothalonil request that ambient monitoring occur in Fresno County for 6 consecutive weeks between May 26 and July 6, 2002. Five sampling sites will be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). At each site, 24 discrete 24-hour samples will be collected, Monday through Friday (4 samples/week), during the 6-week sampling period. Background samples will be collected at the ARB air monitoring site in Fresno. Collocated (replicate) samples will be collected for six dates (each Wednesday) at each sampling location.

The sites will be selected by ARB personnel from areas of historic use of chlorothalonil in Fresno County. Sites will be selected for their proximity to the historic use areas with considerations for both accessibility and security of the sampling equipment. ARB understands that DPR staff will verify and quantify the actual use of chlorothalonil that takes place during the study when the information becomes available.

Application Monitoring

The use pattern for chlorothalonil suggests that application-site monitoring should be conducted in Fresno County sometime during the ambient study, and that the monitoring be associated with an application of chlorothalonil at the highest use rate of approximately 5.0 pounds active ingredient per acre. The exact application monitoring schedule will vary based on the type and length of application but will follow the schedule guidelines outlined below in Table 1. Ideally, the monitoring study will include samples taken before, during and for approximately 72 hours following application.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

Sample period begins:	**Sample duration time**
Background (pre-application)	24 hours
During application	Length of application time
End of application	1 hour (or up to 1 hour before sunset) [1]
1 hour post-application	2 hours (or up to 1 hour before sunset) [1]
3 hour post-application	3 hours (or up to 1 hour before sunset) [1]
6 hour post-application	6 hours (or up to 1 hour before sunset) [1]
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

1 These sample duration times will be adjusted depending on length of application and time of sunset.
2 All overnight samples must include the period from one hour before sunset to one hour after sunrise. If the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application.

Occasionally, a pesticide application may occur over the course of two or more days. In these instances samples are collected during the first daily application followed by a sample from the end of application to 1 hour before sunset (if applicable), followed by an overnight sample ending at either the start of application or 1 hour after sunrise the next morning, whichever is first (same for third or more application days). If the day-2 application does not start at or before '1 hour after sunrise' and the expected time between '1 hour after sunrise' and the start of application is more than 2 hours then an additional sample will be collected during this period. Following the end of the final application, samples are collected according to the above schedule, starting with the 1-hour sample. As stated above, if the application extends beyond "1 hour before sunset" then the overnight sample will be started at the end of application (i.e., no 1, 2, or 3 hour samples will be collected post application in this case).

A minimum of 8 samplers will be positioned, one on each side of the field and one in each corner. A ninth sampler will be collocated at one position (downwind). Background (before application) samples should collected for 24 hours. Ideally, samplers should be placed at 20 meters from the field.

The exact location of the application monitoring study has not yet been determined. ARB staff will contact the County Agricultural Commissioner's offices in the Fresno County area to coordinate the selection of a study site and the test dates. The County Agricultural Commissioner's staff will make initial contact with, or will at least provide a list of local contacts for growers, applicators, and/or pesticide control advisers that may be willing to cooperate in conducting the study. Monitoring sites are arranged with the voluntary cooperation of growers

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and applicators. ARB staff will investigate contacts until a cooperative grower is found and an appropriate site is selected. Permission to conduct the study will be obtained from the application plot land-owner and owners of adjacent land where samplers will be positioned.

Candidate fields for application monitoring will be 10 acres or larger. The crop type or specific application method for the application study were not specified by the DPR. However, the DPR recommended that, "monitoring should occur at a site using the highest allowed use rates (i.e., 5 pounds AI per acre for chlorothalonil)".

We will provide the following information in the monitoring report:

1) An accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field,
2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, etc.,
3) meteorological data collected at a minimum of 15 minute intervals including wind speed and direction, humidity, and comments regarding degree of cloud cover,
4) the elevation of each sampling station with respect to the field and
5) the orientation of the field with respect to North (identified as either true or magnetic north).
6) The start and end time of the application each day.

III. Analysis

The sampling and analytical methods used for this study are based on methods used to conduct similar monitoring (for DPR) in 1992. The "Standard Operating Procedure for the Analysis of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (Chlorothalonil) in Ambient Air" (May 17, 2002 draft version) are included as Attachment II. The procedures consist of extraction of the exposed XAD-2 resin with an organic solvent followed by GC/MS analysis. DPR requested a target 24-hour estimated quantitation limit (EQL) of 1.0 ng/m^3. The EQL actually achieved by the method was 2.3 ng/m^3.

IV. Quality Assurance

Field Quality Control for the ambient monitoring will include:

1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air at the background monitoring site (ARB Fresno site) for 24 hour periods at 3.0 sLpm (i.e., collocated with a background sample). One field spike each will be collected during weeks 1, 3, 4 and 6.

2) Four trip spikes prepared at the same level as the field spikes.

3) Four lab spikes prepared at the same level as the field and trip spikes.

4) Collocated (replicate) samples will be taken for six dates (each Wednesday) at each sampling location.

5) A Trip blank will be obtained each week of sampling.

Field Quality Control for the application monitoring will include:

1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air during background monitoring at the application site for the same duration as the background samples at 3.0 sLpm (i.e., collocated with background samples).

2) Four trip spikes prepared at the same level as the field spikes.

3) Four lab spikes prepared at the same level as the field and trip spikes.

4) Collocated (replicate) samples will be taken for all samples at one of the sampling locations (downwind).

5) One trip blank will be obtained during the study.

A chain of custody sheet will accompany all samples. Mass flow meters will be calibrated by the ARB Standards Laboratory. The flow rate of each sampler will be audited by the ARB Quality Assurance Section prior to the monitoring studies.

V. Sample Labeling

Samples for the application study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:
Location is designated as north 1, 2 or 3 (N1, N2, N3), west (W), south 1, 2 or 3 (S1, S2, S3), and east (E). These designations can be revised as necessary depending on the configuration of the field.

Chlorothalonil is designated as C.

Sampling period is designated as B (for background) or 1 through 9 (# of periods can vary).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Examples:
- S2-C-B-S (South2, Chlorothalonil, background, sample)
- S2-C-B-FS (South2, Chlorothalonil, background, field spike)
- S2-C-1-S (South2, Chlorothalonil, sampling period 1, sample)
- S2-C-1-CO (South2, Chlorothalonil, sampling period 1,collocated)

Samples for the ambient study will be labeled using the following format:

Location-Chemical-Sampling Period-Type of Sample

Where:
Location is designated by 3-letters. The designations will be defined after the sites have been chosen.

Chlorothalonil is designated as C.

Sampling period is designated as 1 through 24 (e.g., 24 periods in 6 weeks).

The type of sample is designated as S (sample), CO (collocated), TB (trip blank), TS (trip spike), and FS (field spike).

Example: ARB-C-1-S (ARB Fresno site, Chlorothalonil, period 1, sample)
ARB-C-1-CO (ARB Fresno site, Chlorothalonil, period 1, collocated)

VI. Personnel

ARB personnel involved with coordinating and conducting the field activities will consist of staff of the Air Quality Surveillance Branch, ARB.

VII. Safety Recommendations

The DPR's 'Monitoring Recommendations' include the following safety recommendations.

"The chlorothalonil product labels alert that chlorothalonil is hazardous to humans and domestic animals. Chlorothalonil is corrosive, causes irreversible eye damage, and may cause allergic reactions in some individuals with prolonged or repeated skin contact. Inhalation may be fatal. Chlorothalonil products may be harmful if swallowed or absorbed through the skin."

"The label advises that applicators, mixers, loaders and other handlers must wear: long sleeve shirt and long pants, chemical resistant gloves, shoes and socks,

protective eyewear, and a dust/mist filtering mask. The restricted-entry interval varies by product from 12 to 48 hours. Monitoring personnel should refer to the label of the product used and should use proper protective equipment to prevent exposure to the dust or spray mist."

MANIFOLD SAMPLER

01/29/02

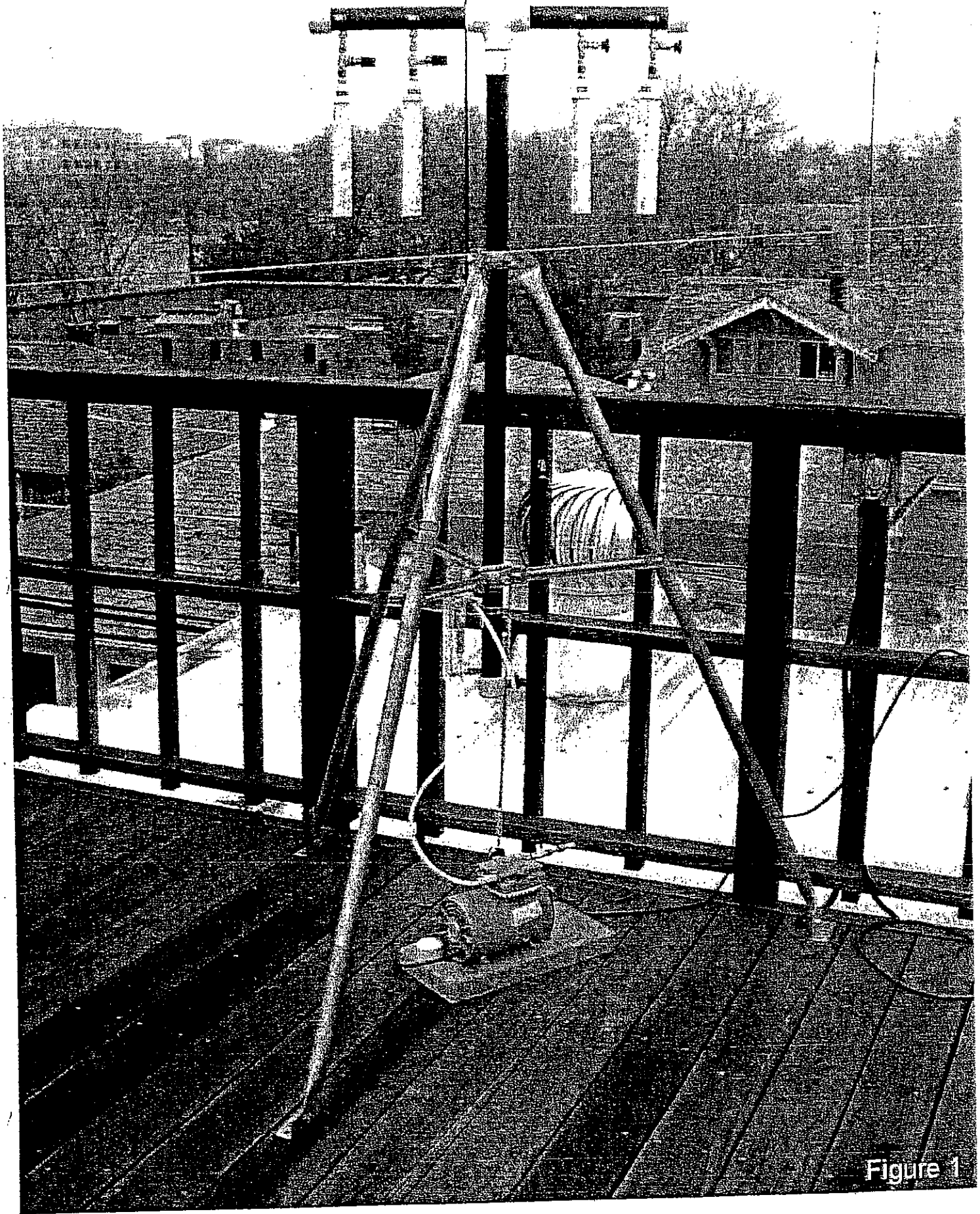

Figure 1

Attachment III

Pesticide Sampling Procedures for Adsorbent Tubes
For Ambient Monitoring Studies

Pesticide Ambient Sampling Procedures
For Adsorbent Tubes

Overview:

-Collect samples over the six week sampling period; 24 hour samples; Four sampling periods per week per site; Five sampling sites plus an urban background site (ARB Fresno station).

-Collect a collocated sample from each site each Wednesday,

-Submit 1 trip blank per week,

-With the trip blank there normally will be 31 samples collected per week,

-4 field spikes will be run at the ARB site (time collocated exactly with the ambient sample. The field spikes will be distributed over the monitoring period (e.g., 1 per week on weeks 1, 3, 4, and 6). A trip spike will also accompany each field spike. These field and trip spikes will be logged in and shipped along with the regular samples. The field and trip spikes will be kept on dry ice during transport to and storage in the field.

-All samples are stored either in an ice-chest on dry ice or in a freezer,

-The field log sheet is filled out as the sampling is conducted. The originals stay in the field binder. Please include a copy with sample shipments. All QA samples must be logged onto the log sheet,

-The chain of custody (COC) forms are filled out prior to sample shipment; the originals are shipped with the samples; make and retain copies if desired (not necessary),

-(Disregard if samples are driven back to Sacramento) The samples are shipped by UPS, next day delivery, to 13th and T. This is normally done each Monday. The original chain of custody sheets must accompany the samples. The samples are shipped on 5 pounds of dry ice. Review the COCs and log sheet to insure that all documentation is correct and that the appropriate QA samples have been included.

Sampling Procedure:

Materials that will be needed on the roof to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -0 to 5 sLpm mass flow meter (MFM) with battery

Figure out your route for sampling the six locations and try to keep this the same throughout

the study. In general, try to make each sampling period 24 hours; e.g., if start time is 11:10 then end time should be 11:10. (round off to the nearest 5 minutes.) The sample period may not always be exactly 24 hours; but that is the target time frame.

Preparation and Set-up

On the way to the first site, plug the MFMs into the batteries. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFMs plugged in until the last sample for the day is taken; then unplug for the night to minimize drop in battery charge. Recharge the batteries once per week to be on the safe side.

Upon arrival at the site, check in if needed. Fill out the sample labels for that site. I suggest a backpack and/or fannypacks to carry the stuff to the roof.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Perform the leak check on each sample line by placing a plastic tube cap over the inlet of the cartridge (with the pump on). The rotameter ball should fall to zero. The leak check should be performed before setting the flows with the MFMs.

Using the 5 sLpm MFM set the flow rate exactly to 3.0 sLpm.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, any comments and the weather conditions.

Sample collection and Shipment

Measure (do not re-set) the flow rates at the end of the sampling period with the MFMs; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each day (6) in a zip-lock bag and place on dry ice in a cooler or in a freezer. While driving the route the collected samples need to be kept on dry ice.

Collect the collocated (duplicate) samples from each site every Wednesday. These should be started and stopped at the same times as the regular samples.

Collect a trip blank (TB) once per week,while at one of the field sites. It doesn't matter

which site (or which day) but note it in the comment section of the log sheet. The TB is collected by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

APPENDIX II

2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile (Chlorothalonil)
Method Development and Analytical Results for Ambient Air Monitoring Samples

California Environmental Protection Agency

Air Resources Board

2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile (Chlorothalonil) Method Development and Analytical Results for Ambient Air Monitoring Samples

DATE: August 2002

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1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct ambient air monitoring for 2,4,5,6-tetrachloro-1, 3-benzenedicarbonitrile (chlorothalonil). This report covers the method development and analytical and quality assurance results for chlorothalonil during a six (6) week period in Fresno County. DPR requested a method estimated quantitation limit (EQL) of one (1) nanogram per cubic meter (ng/m^3). The EQL achieved during this project was 2.25 ng/m^3

2.0 METHOD DEVELOPMENT

2.1 Overview

XAD-2 cartridges are used for ambient air sampling. Sample cartridges are stored at or below four (4) degrees centigrade (°C) before extraction. Sample cartridges are extracted with three (3) milliliters (ml) of methylene chloride (DCM) and desorbed in an ultrasonic bath. Sample extracts are analyzed using a gas chromatograph/mass selective detector (GC/MSD), which is operated in the selected ion-monitoring mode (SIM). Sample analysis and quantitation used the internal standard aldrin $^{13}C_4$, which was added to the extracts before GC/MSD analysis. Estimated quantitation levels for this method, based on 4.3 cubic meters (m^3) of air collected, and a final extract volume of three (3) ml, is 2.25 ng/m^3. Appendix A contains the standard operating procedure (SOP) for chlorothalonil.

2.2 Instrument Reproducibility

Five (5) individual injections of two (2) microliters (µl) each were made of chlorothalonil at three (3) concentrations (low, medium, and high) in order to establish the reproducibility of the instrument. Table 1 shows the results for the three levels with the average and standard deviation for each level.

2.3 Calibration Curve

Laboratory staff used standard concentrations of approximately 3, 6, 15, 31, 62, 94, and 125 ng/ml to produce a seven (7) point calibration curve. All calibration curves performed had a r^2 (variance) greater than or equal to 0.995. Laboratory staff performed calibrations at the beginning of the monitoring program, after instrument maintenance, after remaking of internal standard, and whenever the continuing calibration verification standard (CCV) did not fall within ± 25 percent (%) of expected value.

2.4. *Minimum Detection Limit (MDL)*

The MDL calculation follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (5.0 ng/ml), the MDL and EQL for a three (3) ml extract is calculated as follows:

s = the standard deviation of the concentration calculated for the seven replicate spikes.
For chlorothalonil: s = 0.2046 ng/ml

$$MDL = (3.14) \times (s) = (3.14) \times (0.2046) = 0.643 \text{ ng/ml.}$$

$$EQL = (5) \times (MDL) = (5) \times (0.6432) = 3.22 \text{ ng/ml}$$

*EQL for total ng/sample = 9.66 ng/sample**

** assuming a 3 ml final extract volume*

Based on a total collection volume of 4.3 m^3 the EQL would be 2.25 ng/m^3. Staff report results above the EQL to three (3) significant figures. Results below the EQL but greater than or equal to the MDL are reported as detected (DET). Results less than MDL are reported as <MDL.

2.5. *Collection and Extraction Efficiency (Recovery)*

Six (6) XAD-2 cartridges were used to determine method field recovery. The primary sections (front bed) of three (3) sample cartridges were spiked with 20.2 ng of chlorothalonil standard and three (3) others with 101 ng. The spiked tubes were placed on field samplers and sampled at an airflow of approximately three (3) liters per minute (lpm) for 24 hours at ambient temperature. The XAD-2 was removed from the primary section of the XAD-2 cartridge and using three (3) ml of DCM was desorbed using an ultrasonic bath. After extraction and filtration, internal standard was added and the extract was analyzed by GC/MSD. The average recoveries and standard deviations for chlorothalonil were as follows: An average recovery of 17.9 $\pm$ 2.67 ng was achieved for the low level spikes, while an average recovery of 89.8 $\pm$ 4.08 ng was achieved for the high level spikes.

2.6. *Storage Stability*

Laboratory staff completed a storage stability study which ran for 24 days with cartridges being tested at 0, 6, 13, and 24 days. The average percent recovery and standard deviation for each group was 92 $\pm$ 18, 115 $\pm$ 4.8, 101 $\pm$ 11, and 106 $\pm$ 4.5, respectively. Chlorothalonil, spiked at 52 ng on XAD-2 cartridges, was stable for up to 24 days when stored in a freezer at -20 ° C. Laboratory staff analyzed all field samples within 21 days of collection.

2.7. Breakthrough

Three (3) XAD-2 cartridges were spiked with one(1) µg of chlorothalonil to evaluate analyte breakthrough. Air was collected at approximately three (3) lpm for 24 hours. Chlorothalonil was not detected in the secondary section of the XAD-2 cartridges. Average recovery for chlorothalonil from the primary sections was 92 ± 6.95%.

3.0 CHLOROTHALONIL AMBIENT AIR MONITORING SAMPLE RESULTS.

The laboratory received a total of 163 ambient samples plus six (6) field spikes, six (6) field blanks, and six (6) trip spikes from May 31, 2002 to July 3, 2002. Table 2 presents the results of the analysis of the chlorothalonil ambient air samples by site.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzed a system blank with each analytical batch, after each CCV, after every tenth sample and after samples containing high levels of chlorothalonil or co-extracted contaminants. Staff defined the analytical batch as all the samples extracted together, but not to exceed twenty (20) samples. The system blank was run to ensure the solvent and instrument did not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This was an XAD-2 cartridge prepared and analyzed as described for the ambient samples. Laboratory staff analyzed 11 method blanks during this project. All method blanks were less than the MDL.

4.3 Laboratory Control Samples (LCS)

Laboratory staff analyzed a LCS with each analytical batch. The stock standard used to prepare the LCS came from a different source or was a different lot number than the stock standard used for method calibration. A LCS was an XAD-2 cartridge spiked with 50 ng of chlorothalonil. The LCS was extracted and analyzed as described for the samples. The LCS recoveries averaged 111% with a standard deviation of 8.80%. The acceptable LCS range was 42.1 to 68.5 ng.

4.4 Continuing Calibration Verification Standards (CCV)

Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth (10) sample and at the end of an analytical batch.

The CCV must be within ± 25% of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV for each analytical batch is 15 ng/ml.

4.5 Laboratory Duplicates

No laboratory duplicates were run with this project.

5.0 FIELD, TRIP, AND LABORATORY SPIKES AND TRIP BLANKS

During the Fresno County project six (6) sets of laboratory, trip, and field spikes along with six (6) trip blanks were analyzed. Laboratory staff prepared one set of spikes at 17.33 ng/ml of chlorothalonil, each week during the six-week project.

5.1 Laboratory Spikes

Table 3 presents the results of the laboratory spikes. The average chlorothalonil recovery was 90.42% with a standard deviation of 26.02%. The laboratory spike analyzed during week three of this project had a very low recovery (40.85%) for chlorothalonil, which resulted in the high standard deviation. If laboratory staff removes this result from the average and standard deviation calculation, the new average recovery would be 100.34% with a standard deviation of 8.15%.

5.2 Trip Spikes

Table 3 presents the results of the trip spikes. The average recovery for chlorothalonil was 98.70% with a standard deviation of 7.73%. The recovery for the trip spike run during week three was 91.56%. If this result was removed from the calculation, the average recovery would be 100.13% with a standard deviation of 3.87%.

5.3 Field Spikes

Table 3 presents the results of the field spikes. The spikes were placed on a sampler at the ARB ambient air monitoring station in Fresno. The average recovery of the field spikes was 84.45% with a standard deviation of 21.75%. The field spike analyzed during week three had a very low recovery (45.75%) for chlorothalonil, which resulted in the high standard deviation. If laboratory staff removes this result from the average and standard deviation calculation, the new average recovery would be 92.19% with a standard deviation of 2.39%. The chlorothalonil quantitations for the ARB site run concurrently with the field spikes generally showed values less than the EQL, only FRS-14 had a value greater then the EQL (61.80 ng/sample). Because of these low background levels, no corrections were made to the field spike recoveries.

5.4 Trip Blanks

Table 3 presents the results of the trip blanks. All six (6) trip blanks received during this project had results less than the MDL.

6.0 DISCUSSION

During the project, 163 ambient samples were analyzed. Twenty-one samples had results greater than the EQL of 9.66 ng/sample. The concentrations ranged from 9.93 to 61.80 ng/sample. Seventy-three samples had results reported as detected. No problems or anomalies occurred during these analyses.

Laboratory staff analyzed six (6) sets of field spikes during this project. Although recoveries were generally good, it was noted that recoveries for the lab spike and field spike sampled during week three were much lower than expected, 40.85% and 45.75% respectively. It is suspected that either the cartridges were not spiked correctly or during sample extraction, analyte was lost. The trip spike for week three had a recovery of approximately 92%. Since all three spikes (laboratory, trip, and field) were extracted and analyzed in the same analytical batch, it is more likely that the cartridges were spiked incorrectly. If these results were removed from the standard deviation calculation, the standard deviation would improve significantly.

All other project QC was acceptable and no other problems or anomalies were observed during this project.

Table 1: Instrument Reproducibility

Chlorothalonil (ng/ml)			
Sample Number	Low Level	Medium Level	High Level
1	7.18	34.9	93.7
2	6.85	38.0	85.2
3	7.43	36.7	86.5
4	7.45	38.1	90.3
5	6.90	38.1	84.1

Average	7.162	37.170	87.980
SD	0.2833	1.3980	3.9840

Notes:
ml Milliliters
ng Nanograms
SD Standard deviation

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
CES	6	CES-C-01	5/31/02	6/5/02	<MDL
	14	CES-C-02	5/31/02	6/5/02	<MDL
	15	CES-C-02C	5/31/02	6/6/02	DET
	24	CES-C-03	5/31/02	6/6/02	<MDL
	31	CES-C-04	6/7/02	6/11/02	DET
	41	CES-C-05	6/7/02	6/11/02	1.93E+01
	42	CES-C-05C	6/7/02	6/11/02	1.82E+01
	51	CES-C-06	6/7/02	6/12/02	1.24E+01
	57	CES-C-07	6/7/02	6/12/02	<MDL
	64	CES-C-08	6/14/02	6/18/02	1.37E+01
	74	CES-C-09	6/14/02	6/19/02	<MDL
	75	CES-C-09C	6/14/02	6/19/02	<MDL
	84	CES-C-10	6/14/02	6/20/02	<MDL
	90	CES-C-11	6/14/02	6/20/02	<MDL
	97	CES-C-12	6/21/02	7/3/02	<MDL
	107	CES-C-13	6/21/02	7/3/02	<MDL
	108	CES-C-13C	6/21/02	7/3/02	<MDL
	117	CES-C-14	6/21/02	7/9/02	3.29E+01
	123	CES-C-15	6/21/02	7/9/02	1.12E+01
	130	CES-C-16	6/28/02	7/9/02	1.58E+01
	140	CES-C-17	6/28/02	7/10/02	2.49E+01
	141	CES-C-17C	6/28/02	7/10/02	2.72E+01
	150	CES-C-18	6/28/02	7/10/02	<MDL
	157	CES-C-19	6/28/02	7/10/02	<MDL
	166	CES-C-20	7/3/02	7/11/02	2.56E+01
	174	CES-C-21	7/3/02	7/11/02	DET
	175	CES-C-21C	7/3/02	7/11/02	DET

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
FRS	3	FRS-C-01	5/31/02	6/5/02	<MDL
	10	FRS-C-02	5/31/02	6/5/02	<MDL
	11	FRS-C-02C	5/31/02	6/5/02	DET
	22	FRS-C-03	5/31/02	6/6/02	<MDL
	28	FRS-C-04	6/7/02	6/11/02	<MDL
	37	FRS-C-05	6/7/02	6/11/02	DET
	38	FRS-C-05C	6/7/02	6/11/02	DET
	49	FRS-C-06	6/7/02	6/12/02	DET
	55	FRS-C-07	6/7/02	6/12/02	<MDL
	61	FRS-C-08	6/14/02	6/18/02	<MDL
	70	FRS-C-09	6/14/02	6/18/02	<MDL
	71	FRS-C-09C	6/14/02	6/18/02	<MDL
	82	FRS-C-10	6/14/02	6/19/02	<MDL
	88	FRS-C-11	6/14/02	6/20/02	<MDL
	94	FRS-C-12	6/21/02	7/3/02	DET
	103	FRS-C-13	6/21/02	7/3/02	DET
	104	FRS-C-13C	6/21/02	7/3/02	DET
	115	FRS-C-14	6/21/02	7/4/02	6.18E+01
	121	FRS-C-15	6/21/02	7/9/02	<MDL
	127	FRS-C-16	6/28/02	7/9/02	DET
	136	FRS-C-17	6/28/02	7/10/02	DET
	137	FRS-C-17C	6/28/02	7/10/02	DET
	148	FRS-C-18	6/28/02	7/10/02	DET
	155	FRS-C-19	6/28/02	7/10/02	<MDL
	161	FRS-C-20	7/3/02	7/11/02	DET
	170	FRS-C-21	7/3/02	7/11/02	DET
	171	FRS-C-21C	7/3/02	7/11/02	DET

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
HES	5	HES-C-01	5/31/02	6/5/02	<MDL
	12	HES-C-02	5/31/02	6/5/02	<MDL
	13	HES-C-02C	5/31/02	6/5/02	<MDL
	23	HES-C-03	5/31/02	6/6/02	<MDL
	30	HES-C-04	6/7/02	6/11/02	<MDL
	39	HES-C-05	6/7/02	6/11/02	<MDL
	40	HES-C-05C	6/7/02	6/11/02	<MDL
	50	HES-C-06	6/7/02	6/12/02	<MDL
	56	HES-C-07	6/7/02	6/12/02	<MDL
	63	HES-C-08	6/14/02	6/18/02	<MDL
	72	HES-C-09	6/14/02	6/19/02	<MDL
	73	HES-C-09C	6/14/02	6/19/02	<MDL
	83	HES-C-10	6/14/02	6/20/02	<MDL
	89	HES-C-11	6/14/02	6/20/02	<MDL
	96	HES-C-12	6/21/02	7/3/02	<MDL
	105	HES-C-13	6/21/02	7/3/02	<MDL
	106	HES-C-13C	6/21/02	7/3/02	<MDL
	116	HES-C-14	6/21/02	7/9/02	DET
	122	HES-C-15	6/21/02	7/9/02	<MDL
	129	HES-C-16	6/28/02	7/9/02	<MDL
	138	HES-C-17	6/28/02	7/10/02	<MDL
	139	HES-C-17C	6/28/02	7/10/02	<MDL
	149	HES-C-18	6/28/02	7/10/02	<MDL
	156	HES-C-19	6/28/02	7/10/02	<MDL
	165	HES-C-20	7/3/02	7/11/02	DET
	172	HES-C-21	7/3/02	7/11/02	DET
	173	HES-C-21C	7/3/02	7/11/02	DET

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
HUS	9	HUS-C-01	5/31/02	6/5/02	DET
	20	HUS-C-02	5/31/02	6/6/02	<MDL
	21	HUS-C-02C	5/31/02	6/6/02	DET
	27	HUS-C-03	5/31/02	6/6/02	<MDL
	34	HUS-C-04	6/7/02	6/11/02	<MDL
	47	HUS-C-05	6/7/02	6/12/02	DET
	48	HUS-C-05C	6/7/02	6/12/02	DET
	54	HUS-C-06	6/7/02	6/12/02	DET
	60	HUS-C-07	6/7/02	6/12/02	DET
	67	HUS-C-08	6/14/02	6/18/02	<MDL
	80	HUS-C-09	6/14/02	6/19/02	<MDL
	81	HUS-C-09C	6/14/02	6/19/02	<MDL
	87	HUS-C-10	6/14/02	6/20/02	DET
	93	HUS-C-11	6/14/02	6/21/02	<MDL
	100	HUS-C-12	6/21/02	7/3/02	DET
	113	HUS-C-13	6/21/02	7/4/02	DET
	114	HUS-C-13C	6/21/02	7/4/02	DET
	120	HUS-C-14	6/21/02	7/9/02	DET
	126	HUS-C-15	6/21/02	7/9/02	DET
	133	HUS-C-16	6/28/02	7/9/02	DET
	146	HUS-C-17	6/28/02	7/10/02	DET
	147	HUS-C-17C	6/28/02	7/10/02	DET
	154	HUS-C-18	6/28/02	7/10/02	DET
	160	HUS-C-19	6/28/02	7/10/02	DET
	169	HUS-C-20	7/3/02	7/11/02	DET
	180	HUS-C-21	7/3/02	7/11/02	DET
	181	HUS-C-21C	7/3/02	7/11/02	DET

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
WES	7	WES-C-01	5/31/02	6/5/02	DET
	16	WES-C-02	5/31/02	6/6/02	<MDL
	17	WES-C-02C	5/31/02	6/6/02	<MDL
	25	WES-C-03	5/31/02	6/6/02	1.86E+01
	32	WES-C-04	6/7/02	6/11/02	DET
	43	WES-C-05	6/7/02	6/11/02	DET
	44	WES-C-05C	6/7/02	6/12/02	DET
	52	WES-C-06	6/7/02	6/12/02	DET
	58	WES-C-07	6/7/02	6/12/02	DET
	65	WES-C-08	6/14/02	6/18/02	DET
	76	WES-C-09	6/14/02	6/19/02	<MDL
	77	WES-C-09C	6/14/02	6/19/02	<MDL
	85	WES-C-10	6/14/02	6/20/02	<MDL
	91	WES-C-11	6/14/02	6/20/02	DET
	98	WES-C-12	6/21/02	7/3/02	DET
	109	WES-C-13	6/21/02	7/3/02	1.48E+01
	110	WES-C-13C	6/21/02	7/3/02	1.72E+01
	118	WES-C-14	6/21/02	7/9/02	1.42E+01
	124	WES-C-15	6/21/02	7/9/02	1.14E+01
	131	WES-C-16	6/28/02	7/9/02	DET
	142	WES-C-17	6/28/02	7/10/02	<MDL
	143	WES-C-17C	6/28/02	7/10/02	<MDL
	151	WES-C-18	6/28/02	7/10/02	DET
	152	WES-C-18C	6/28/02	7/10/02	1.04E+01
	158	WES-C-19	6/28/02	7/10/02	DET
	167	WES-C-20	7/3/02	7/11/02	1.69E+01
	176	WES-C-21	7/3/02	7/11/02	DET
	177	WES-C-21C	7/3/02	7/11/02	DET

Table 2: Ambient Air Monitoring Results
Fresno County 2002

Site	Log Number	Sample ID	Date Received	Date Analyzed	Chlorothalonil (ng/sample)
WRS	8	WRS-C-01	5/31/02	6/5/02	<MDL
	18	WRS-C-02	5/31/02	6/6/02	<MDL
	19	WRS-C-02C	5/31/02	6/6/02	<MDL
	26	WRS-C-03	5/31/02	6/6/02	<MDL
	33	WRS-C-04	6/7/02	6/11/02	DET
	45	WRS-C-05	6/7/02	6/12/02	DET
	46	WRS-C-05C	6/7/02	6/12/02	DET
	53	WRS-C-06	6/7/02	6/12/02	DET
	59	WRS-C-07	6/7/02	6/12/02	DET
	66	WRS-C-08	6/14/02	6/18/02	<MDL
	78	WRS-C-09	6/14/02	6/19/02	<MDL
	79	WRS-C-09C	6/14/02	6/19/02	<MDL
	86	WRS-C-10	6/14/02	6/20/02	DET
	92	WRS-C-11	6/14/02	6/20/02	DET
	99	WRS-C-12	6/21/02	7/3/02	DET
	111	WRS-C-13	6/21/02	7/4/02	DET
	112	WRS-C-13C	6/21/02	7/4/02	1.01E+01
	119	WRS-C-14	6/21/02	7/9/02	DET
	125	WRS-C-15	6/21/02	7/9/02	DET
	132	WRS-C-16	6/28/02	7/9/02	DET
	144	WRS-C-17	6/28/02	7/10/02	1.02E+01
	145	WRS-C-17C	6/28/02	7/10/02	9.93E+00
	153	WRS-C-18	6/28/02	7/10/02	DET
	159	WRS-C-19	6/28/02	7/10/02	DET
	168	WRS-C-20	7/3/02	7/11/02	DET
	178	WRS-C-21	7/3/02	7/11/02	DET
	179	WRS-C-21C	7/3/02	7/11/02	DET

Table 2 Notes: Ambient Monitoring Results, Fresno County 2002

If analytical result is ≥ MDL and < EQL it is reported in the table as detected (DET). Levels at or above the EQL are reported as the actual measured value and are reported to three significant figures.

<MDL = Less than method detection limit (1.93 ng/sample)

ng = nanogram

Sample ID (Sample identification) numbers ending with the letter C (for example: WRS-C-17C) are collocated samples for the samples with the corresponding number.

Site location identification:

CES:	Cantua Creek Elementary School
FRS:	Fresno APCD monitoring site
HES:	Helm Elementary School
HUS:	Huron Elementary School
WES:	Westside Elementary School
WRS:	Westside Research and Extension

Table 3: XAD-2 Cartridge Spike and Trip Blank Results
Fresno County 2002

Quality Control Type	Laboratory ID	Date Analyzed	Measured Chlorothalonil amount (ng/sample)	Percent Recovery
Lab Spike (52ng/sample)	L6302	6/5/02	45.51	87.52
	L610	6/11/02	49.41	95.02
	L617	6/17/02	21.24	40.85
	L701	7/3/02	55.98	107.7
	L0703B	7/9/02	59.19	113.9
	L0708B	7/11/02	50.79	97.67
Trip Spike (52 ng/sample)	C001	6/5/02	52.68	101.3
	C036	6/11/02	45.45	87.40
	C068	6/18/02	47.61	91.56
	C101	7/3/02	56.31	108.3
	C134	7/9/02	53.49	102.9
	C163	7/11/02	52.41	100.8
Field Spike (52 ng/sample)	C004	6/5/02	38.94	74.88
	C029	6/11/02	44.10	84.81
	C061	6/18/02	23.79	45.75
	C095	7/3/02	53.34	102.6
	C128	7/9/02	50.88	97.85
	C162	7/11/02	52.44	100.9
Trip Blank	C002	6/5/02	<MDL	
	C035	6/11/02	<MDL	
	C069	6/18/02	<MDL	
	C102	7/3/02	<MDL	
	C135	7/9/02	<MDL	
	C164	7/11/02	<MDL	

Notes:

ID Identification
<MDL Less than method detection limit
ng Nanograms

Appendix A:

Standard Operating Procedure for Chlorothalonil

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure
Sampling and Analysis of 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile (Chlorothalonil) in Ambient Air

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

August 2002

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This is a gas chromatography/mass selective detector (GC/MSD) method for the determination of 2,4,5,6-tetrachloro-1,3-benzenecarbonitrile (chlorothalonil) from ambient air samples. The method was adapted from the California Air Resources Board Standard Operating Procedure for the Analysis of Chlorothalonil in Ambient Air dated January 1992. The Department of Pesticide Regulation requested an estimated quantitation limit (EQL) of one (1) nanogram per cubic meter (ng/m^3) for this project.

2. SUMMARY OF METHOD

Ambient air is collected on XAD-2 cartridges. Sample cartridges are stored at four (4) degrees centigrade (°C) or lower prior to extraction. Samples cartridges are extracted using methylene chloride and an ultrasonic bath. Samples analysis is performed using a GC/MSD in the selected ion-monitoring mode (SIM). Sample analysis and quantitation uses the internal standard Aldrin $^{13}C_4$, which is added to each extract prior to GC/MSD analysis. Estimated quantitation levels for this method range from approximately 2.5 nanogram per cubic meter to 90 nanogram per cubic meter (ng/m^3) prior to sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 cartridges that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting pesticide components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

Hewlett Packard 5890 Series II gas chromatograph:

Detector: 300° C
Injector: 250° C
Column: Restek Rtx-5MS, 30 meters, 0.32 mm i.d., 0.25 µm film thickness, or equivalent
Temperature Program:
Initial Temperature: 50° C for 1 minute
Ramp 1: 50 to 175° C at 50° C per minute hold for 1 minute
Ramp 2: 175 to 250° C at 25° C per minute hold for 0 minutes
Final Ramp: 250 to 300° C at 50° C per minute hold for 3 minutes

Splitter opens at 1.0 minute
Carrier gas: Helium at 1.5 ml/minute constant flow mode

Hewlett Packard 5972 mass selective detector:
Acquisition Mode: SIM
Masses: 264, 266, and 268 for chlorothalonil from 5 to 7.45 minutes
Masses: 265, 267, 269 for Aldrin $^{13}C_4$ from 7.45 to 12 minutes

Tune File: PFTBA Autotune at maximum sensitivity

B. Auxiliary Apparatus

XAD-2 cartridges (SKC cat # 226-30-6) or equivalent
Glass amber vials, 2-ml capacity with septum caps.
Sonicator

C. Reagents

Methylene Chloride (B&J brand pesticide grade or equivalent)
Acetone (B&J brand reagent grade or equivalent)
Chlorothalonil 98.5% pure (Chem Service Inc. PS-1020)
Aldrin $^{13}C_4$ 99% pure, 100 µg/ml (Cambridge Isotopes Laboratories Inc. CLM-3347)

D. Gases

Compressed Helium Grade 5 or better

5. SAMPLE COLLECTION

a) Samples are collected in the field with a maximum flow rate of three (3) liters per minute (lpm).
b) After collection the samples are place in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.
c) According to EPA method TO-10A the cartridges should be extracted within seven (7) days. An analyte specific holding time was determined for chlorothalonil. Chlorothalonil is stable for at least 24 days when kept at -20°C. See section 8F for storage stability summary.

6. SAMPLE EXTRACTON

a) Prepare a method blank and laboratory control sample (LCS) cartridge with every batch of field samples not to exceed twenty (20) samples in an analytical batch.
b) Spike the LCS with 50 ng of chlorothalonil before extraction.

c) Carefully score and break the XAD-2 cartridge just above the glass wool plug and spring on the primary section.
d) Remove the glass wool plug using forceps.
e) Pour the XAD-2 resin from the primary section into the glass vial.
f) Carefully score and break the XAD-2 cartridge just above the glass wool plug on the secondary section.
g) Carefully using 3.0 ml of methylene chloride rinse the inside of the primary section into the glass vial. Cap tightly.
h) Retain the secondary section for later analysis to check for breakthrough.
i) Place all the vials in an ultrasonic bath and sonicate for 30 to 45 minutes.
j) Filter the extract through a 2.7-micron filter into a second vial and store at 4°C or less until ready for analysis.

7. ANALYSIS OF SAMPLES

a) Transfer 1.0 ml of the sample extract to a 1.5-ml autosampler vial. Add 30 ng of internal standard (Aldrin $^{13}C_4$). Sample extract is now ready for analysis.
b) Prior to sample analysis perform a PFTBA autotune using the maximum sensitivity tune option. Evaluate the tune using the criteria listed in Appendix 1. If the tune does not meet the criteria, retune. If the tune continues to be unsuccessful, perform corrective maintenance and then retune.
c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 30 times higher. At least 5 points must be analyzed to establish a calibration curve. Appendix 2 lists the concentrations used when the EQL is approximately 2.5 ng/m^3.
d) Prepare a sample sequence for the GC/MSD. The sequence should include a continuing calibration verification standard (CCV), and a system blank, for every 10 samples analyzed. If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.
e) Because of the nature of the XAD-2 cartridge, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every 5 to 10 samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.
f) A 2-µl injection volume will be used for all analyses.
g) Review and edit the quantitation reports as needed.
h) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.

i) The final results will be adjusted by an appropriate dilution factor and reported in ng/ml.

j) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc (ng/m}^3\text{)} = \frac{\text{Extract Conc (ng/ml) x 3 ml}}{\text{Air Volume Sampled (m}^3\text{)}}$$

k) Given instrument sensitivity and a maximum sample volume of 4.3 m^3 the EQL for this method will be approximately 2.5 ng/m^3.

8. QUALITY ASSURANCE

A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different concentrations of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the Chlorothalonil instrument reproducibility.

TABLE 1
INSTRUMENT REPRODUCIBILITY
CHLOROTHALONIL (ng/ml)

Low Level	Medium Level	High Level
7.18	34.9	93.7
6.85	38.0	85.2
7.43	36.7	86.5
7.45	38.1	90.3
6.90	38.1	84.1

7.1620	37.170	87.980	Average
0.2833	1.3980	3.9840	Std Dev
3.956	3.762	4.528	RSD

B. Linearity

A seven (7) point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 30 times higher are used for Chlorothalonil. The results are used to calculate calibration curves using linear or quadratic regression. An r^2 of 0.995 or higher is required for an initial calibration to be acceptable. See Appendix 2 for an example calibration curve. A CCV will be run at the start of each analytical batch,

and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level standard, the MDL and EQL for Chlorothalonil are calculated as follows:

$$MDL = 3.143*STD$$

$$EQL = 5*MDL$$

STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDL for Chlorothalonil is 0.4487 ng/m^3 using a three-ml extraction volume and a sample collection volume of 4.3 m^3. The calculated EQL for Chlorothalonil is 2.24 ng/m^3.

D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from a different source or lot than the daily calibration standards. The analytical value of the LCS must be within three standard deviations of it's historical mean. If the LCS is outside of limits then the samples in the analytical batch must be reanalyzed.

E. Collection and Extraction Efficiency (Recovery)

Collection and efficiency (recovery) data for chlorothalonil should be established prior to sample analysis. Using two concentration levels (20.2 and 101 ng) the recovery for chlorothalonil was as follows: An average recovery of 17.9 ng with a standard deviation of 2.67 ng was achieved for the low level spikes, while an average recovery of 89.8 ng with a standard deviation of 4.08 ng was achieved for the high level spikes.

F. Storage Stability

Storage stability studies were performed in triplicate using 52 ng chlorothalonil spiked on the primary section of XAD-2 cartridges. The project was run for 24 days with cartridges being tested at 0, 6, 13, 24 days. The average percent recovery and standard deviation for each group was 92 $\pm$ 18, 115 $\pm$ 4.8, 101 $\pm$ 11, and 106 $\pm$ 4.5, respectively. Note that for the day zero group one result was lower than the other two leading to a high standard deviation. This is most likely due to an analyst error with this particular extraction.

G. Breakthrough

Three XAD-2 cartridges were spiked with 1 µg of Chlorothalonil to evaluate analyte breakthrough. Air was collected at approximately 3 lpm for 24 hours. Chlorothalonil was not detected in the back section of the XAD-2 cartridges. Average recovery for chlorothalonil from the front sections was 92%.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Appendix 1

Autotune Criteria

A maximum sensitivity autotune should be performed on the detector each day prior to sample analysis. The autotune report should be evaluated for the following:

1. Any unusual change in the EM voltage
2. Peak width for all tune masses should be between 0.4 amu and 0.6 amu.
3. The relative abundance of tune mass 219.0 should be greater than 25% of tune mass 69.0
4. Isotope abundance ratio for tune mass 70.0 should between 0.54% and 1.6%; isotope abundance ratio for tune mass 220.0 should be between 3.2% and 5.4%.
5. Masses 28 and 18 should be evaluated to check for air leaks in the system.

If autotune criteria are not met the system should be evaluated for problems. After the system problems are corrected the detector should be autotuned prior to sample analysis. Autotune reports should be filed in the instrument autotune folder.

Appendix 2

Calibration Standard Preparation for Chlorothalonil

The certified neat standard used for calibration was purchased from Chem Service Inc., West Chester, Pennsylvania and has the following specification:

Lot No:	276-95A
Expiration date:	February 2007
Chlorothalonil	98.5% pure (solid)

A stock standard with a concentration of approximately 1-milligram (mg) per ml was prepared by weighing 25 mg of chlorothalonil into a 25 ml volumetric flask and bringing to volume with methylene chloride.

Using a serial dilution technique the following calibration standards were prepared in methylene chloride: 3.04, 6.03, 15.0, 31.2, 62.4, 93.6, and 124.8 ng/ml.

A minimum of six standards was used to generate the calibration curve, with the standard at 3.04 ng/ml being the low point. The low point equates to approximately 2.12 ng/m^3.

All standard and sample injection used a volume of 2 µl.

Initial calibration curve acceptance requires a r^2 of at least 0.995.

Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman
1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov

Gray Davis
Governor

MEMORANDUM

TO: Webster Tasat, Manager
Operations Planning and Assessment Section

FROM: Russell Grace, Manager //s//
Special Analysis Section

DATE: September 3, 2002

SUBJECT: METHOD VALIDATION DATA FOR ANALYSIS OF CHLOROTHALONIL

The Special Analysis Section provides laboratory support for the pesticide air monitoring program implemented by the ARB at the request of the Department of Pesticide Regulation. One of the responsibilities of the SAS is laboratory analytical method development. By way of this memo, we are providing you with the method validation data generated in the development of the chlorothalonil analytical method for the 2002 monitoring season. The attached tables contain the currently available data generated to determine the method detection limit (MDL), estimated quantitation limit (EQL), reproducibility, collection and extraction efficiency, storage stability and breakthrough.

All of the method development procedures were summarized in the draft standard operating procedure (SOP) for chlorothalonil. This draft SOP was previously provided to you.

If you have any questions, please contact Mr. Michael Orbanosky at 322-2367 or me at 322-0223.

Attachment
cc: Michael Poore
T. E. Houston
Jim Omand
Kevin Mongar

TABLE 1

METHOD DETECTION LIMIT

Chlorothalonil 2002

Date	Name	Amount Spiked (ng/ml)	Amount quantitated (ng/ml)	Percent Recovery
5/1/2002	MDL01	5.06	4.79	94.66
	MDL02	5.06	4.69	92.69
	MDL03	5.06	5.15	101.78
	MDL04	5.06	5.05	99.80
	MDL05	5.06	4.88	96.44
	MDL06	5.06	5.19	102.57
	MDL07	5.06	5.19	102.57
	Average		4.99	98.6
	Std Dev		0.204	4.04
	MDL (ng/ml)		0.643	
	EQL (ng/ml)		3.22	
	Method EQL (ng/m3)		2.24	

TABLE 2
INSTRUMENT REPRODUCIBILITY

Chlorothalonil (ng/ml)			
Sample Number	Low Level	Medium Level	High Level
1	7.18	34.91	93.73
2	6.85	38.02	85.24
3	7.43	36.70	86.53
4	7.45	38.14	90.33
5	6.90	38.08	84.07
Average	7.16	37.17	87.98
SD	0.28	1.40	3.98
RSD	3.96	3.76	4.53

Notes:

ml	milliliters	RSD	Relative standard deviation
ng	nanograms	SD	Standard Deviation

TABLE 3

COLLECTION AND EXTRACTION EFFICIENCY

Chlorothalonil 2002

Actual Spike amount (ng/sample)	Chlorothalonil amount (ng/sample)	Percent Recovery	Average	St Dev	RSD
20.2	15.42	76.34			
20.2	17.52	86.73			
20.2	20.73	102.62	88.56	13.2	14.95
101	86.49	85.63			
101	94.35	93.42			
101	88.44	87.56	88.87	4.05	4.56

TABLE 4

STORAGE STABILITY

Chlorothalonil 2002

Time (days)	Chlorothalonil Target Amount (ng/sample)	Chlorothalonil Actual Amount (ng/sample)	Percent Recovery	Average	Stdev
0	52.0	52.92	101.77		
	52.0	37.38	71.88		
	52.0	53.43	102.75	92.13	17.54
6	52.0	57.09	109.79		
	52.0	57.87	111.29		
	52.0	53.55	102.98	108.0	4.42
13	52.0	49.32	94.85		
	52.0	60.81	116.94		
	52.0	55.47	106.67	106.2	11.06
24	52.0	51.24	98.54		
	52.0	55.74	107.19		
	52.0	54.39	104.60	103.4	4.44

TABLE 5

BREAKTHROUGH STUDY

Chlorothalonil 2002

Duration (hours)	Primary Bed (ng)	Percent Recovery	Average Percent Recovery	Stdev
24 (1012ng)	861.2	85.10		
	1001.3	98.95		
	930.7	91.97	92.00	6.92
Duration (hours)	Secondary Bed (ng)	Percent Recovery	Average Percent Recovery	Stdev
24 (1012ng)	ND	NA		
	ND	NA		
	ND	NA	NA	NA

Notes:

ug Micrograms
Stdev Standard deviation

APPENDIX III

Field Data Sheets for Chlorothalonil

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
001	FRS-C-1-TS	N/A	05/28/02	0657	N/A	N/A	TRIP SPIKE	PC	AJP
			N/A	N/A	N/A	N/A		N/A	N/A
002	FRS-C-1-FB	N/A	05/28/02	0700	N/A	N/A	FIELD BLANK	PC	AJP
			N/A	N/A	N/A	N/A		N/A	N/A
003	FRS-C-1	MH-3	05/28/02	0717	2952.70	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0630	2975.91	3.07	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
004	FRS-C-1-FS	MG-3	05/28/02	0717	2952.70	2.73	FIELD SPIKE. WHEN PLACING SAMPLES ON USED	K	AJP
			05/29/02	0630	2975.91	2.99	MFM 526. WHEN TAKING OFF USED MFM 5063.	K	AJP
005	HES-C-1	MD-3	05/28/02	0818	2968.21	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0732	2991.43	3.05	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
006	CES-C-1	MJ-3	05/28/02	0901	12516.54	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0818	12539.82	3.03	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
007	WES-C-1	MK-3	05/28/02	0936	2105.12	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0856	2128.45	3.11	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
008	WRS-C-1	MM-3	05/28/02	0958	3231.47	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0920	3254.84	2.95	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
009	HUS-C-1	MB-3	05/28/02	1030	2917.13	2.73	WHEN PLACING SAMPLES ON USED MFM 5286.	K	AJP
			05/29/02	0954	2940.53	2.88	WHEN TAKING SAMPLES OFF USED MFM 5063.	K	AJP
010	FRS-C-2	MH-3	05/29/02	0639	2976.05	2.98	USED MFM 5063 PLACING SAMPLES ON AND TAKING	K	AJP
			05/30/02	0553	2999.29	2.93	SAMPLES OFF.	K	AJP
011	FRS-C-2C	MG-3	05/29/02	0639	2976.05	2.98		K	AJP
			05/30/02	0558	2999.37	2.91		K	AJP
012	HES-C-2	MD-3	05/29/02	0735	2991.50	2.98		K	AJP
			05/30/02	0644	3014.62	2.95		K	AJP
013	HES-C-2C	ME-3	05/29/02	0740	2991.56	2.98		K	AJP
			05/30/02	0649	3014.71	3.00		K	AJP
014	CES-C-2	MJ-3	05/29/02	0821	12539.87	2.98		K	AJP
			05/30/02	0727	12562.97	2.85		K	AJP
015	CES-C-2C	MI-3	05/29/02	0826	12539.95	2.98		K	AJP
			05/30/02	0733	12563.07	3.06		K	AJP
016	WES-C-2	MK-3	05/29/02	0858	2128.49	2.99		K	AJP
			05/30/02	0803	2151.57	2.97		K	AJP
017	WES-C-2C	MF-3	05/29/02	0902	2128.54	2.98		K	AJP
			05/30/02	0809	2151.67	3.15		K	AJP
018	WRS-C-2	MM-3	05/29/02	0923	3254.89	2.98		K	AJP
			05/30/02	0829	3277.99	2.90		K	AJP

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

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Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
019	WRS-C-2C	MT-3	05/29/02	0928	3254.99	2.98		K	AJP
			05/30/02	0834	3278.07	2.94		K	AJP
020	HUS-C-2	MB-3	05/29/02	0957	2940.60	2.98		K	AJP
			05/30/02	0858	2963.60	3.00		K	AJP
021	HUS-C-2C	MU-3	05/29/02	0959	2940.63	2.99		K	AJP
			05/30/02	0903	2963.69	2.96		K	AJP
022	FRS-C-3	MH-3	05/30/02	0556	2999.34	2.98		K	AJP
			05/31/02	0541	3023.09	2.94		K	AJP
023	HES-C-3	MD-3	05/30/02	0646	3014.66	2.98		K	AJP
			05/31/02	0627	3038.34	2.90		K	AJP
024	CES-C-3	MJ-3	05/30/02	0730	12563.03	2.99	DOES NOT MEET 3.0 LPM +/- 10%	K	AJP
			05/31/02	0659	12586.50	2.67		K	AJP
025	WES-C-3	MK-3	05/30/02	0806	2151.62	2.99		K	AJP
			05/31/02	0725	2174.94	2.94		K	AJP
026	WRS-C-3	MM-3	05/30/02	0832	3278.04	2.98		K	AJP
			05/31/02	0741	3301.20	2.95		K	AJP
027	HUS-C-3	MB-3	05/30/02	0900	2963.65	2.98	DOES NOT MEET 3.0 LPM +/- 10%	K	AJP
			05/31/02	0804	2986.70	2.59		K	AJP
028	FRS-C-4	MH-3	06/03/02	0719	3023.10	2.98		K	JW
			06/04/02	0638	3046.42	2.97		K	JW
029	FRS-C-4-FS	MG-3	06/03/02	0719	3023.10	2.97		K	JW
			06/04/02	0638	3046.42	2.96		K	JW
030	HES-C-4	MD-3	06/03/02	0816	3038.35	2.98		K	JW
			06/04/02	0738	3061.73	3.90		K	JW
031	CES-C-4	MJ-3	06/03/02	0901	12586.50	2.99		K	JW
			06/04/02	0822	12609.85	3.04		K	JW
032	WES-C-4	MK-3	06/03/02	0946	2174.98	2.98		K	JW
			06/04/02	0904	2198.29	2.96		K	JW
033	WRS-C-4	MM-3	06/03/02	1009	3301.20	2.98		K	JW
			06/04/02	0932	3324.58	2.98		K	JW
034	HUS-C-4	MB-3	06/03/02	1040	2986.72	2.99		K	JW
			06/04/02	1005	3010.13	2.98		K	JW
035	FRS-C-4-TB	N.A.	06/03/02	1300	N.A.	N.A.		K	JW
			N.A.	N.A.	N.A.	N.A.		N.A.	N.A.
036	FRS-C-4-TS	N.A.	06/03/02	1300	N.A.	N.A.		K	JW
			N.A.	N.A.	N.A.	N.A.		N.A.	N.A.

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
037	FRS-C-5	MH-3	06/04/02	0645	3046.52	3.00		K	JW
			06/05/02	0615	3070.03	2.96		K	JW
038	FRS-C-5C	MG-3	06/04/02	0645	3046.52	2.99		K	JW
			06/05/02	0615	3070.03	2.98		K	JW
039	HES-C-5	MD-3	06/04/02	0743	3061.79	2.98		K	JW
			06/05/02	0708	3085.22	2.90		K	JW
040	HES-C-5C	ME-3	06/04/02	0743	3061.79	2.98		K	JW
			06/05/02	0708	3085.22	2.95		K	JW
041	CES-C-5	MJ-3	06/04/02	0830	12609.98	2.99		K	JW
			06/05/02	0749	12633.30	3.11		K	JW
042	CES-C-5C	MI-3	06/04/02	0830	12609.98	2.98		K	JW
			06/05/02	0749	12633.30	2.96		K	JW
043	WES-C-5	MK-3	06/04/02	0908	2198.35	2.99		K	JW
			06/05/02	0833	2221.76	2.98		K	JW
044	WES-C-5C	MF-3	06/04/02	0908	2198.35	2.98		K	JW
			06/05/02	0833	2221.76	2.93		K	JW
045	WRS-C-5	MM-3	06/04/02	0935	3324.64	2.98		K	JW
			06/05/02	0900	3348.05	2.90		K	JW
046	WRS-C-5C	MT-3	06/04/02	0935	3324.64	2.98		K	JW
			06/05/02	0900	3348.05	2.93		K	JW
047	HUS-C-5	MB-3	06/04/02	1008	3010.20	2.98	POWER OUTAGE (APPROX. 6 HRS)	K	JW
			06/05/02	0929	3028.14	2.98	STRUCTURE FIRE ONE BLOCK AWAY.	K	JW
048	HUS-C-5C	MU-3	06/04/02	1008	3010.20	2.99	SAME AS ABOVE	K	JW
			06/05/02	0929	3028.14	2.91		K	JW
049	FRS-C-6	MH-3	06/05/02	0620	3070.10	2.98		K	JW
			06/06/02	0610	3093.95	2.94		K	JW
050	HES-C-6	MD-3	06/05/02	0711	3085.28	2.98		K	JW
			06/06/02	0703	3109.14	2.97		K	JW
051	CES-C-6	MJ-3	06/05/02	0754	12633.39	2.98		K	JW
			06/06/02	0740	12657.15	2.94		K	JW
052	WES-C-6	MK-3	06/05/02	0837	2221.83	2.97		K	JW
			06/06/02	0813	2245.42	2.99		K	JW
053	WRS-C-6	MM-3	06/05/02	0904	3348.12	2.99		K	JW
			06/06/02	0832	3371.58	2.99		K	JW
054	HUS-C-6	MB-3	06/05/02	0935	3028.24	2.99		K	JW
			06/06/02	0858	3051.63	2.98		K	JW

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

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Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
055	FRS-C-7	MH-3	06/06/02	0614	3094.00	2.98		K	JW
			06/07/02	0548	3117.58	2.97		K	JW
056	HES-C-7	MD-3	06/06/02	0707	3109.20	2.98		K	JW
			06/07/02	0636	3132.68	2.96		K	JW
057	CES-C-7	MJ-3	06/06/02	0743	12657.20	2.98		K	JW
			06/07/02	0711	12680.66	2.86		K	JW
058	WES-C-7	MK-3	06/06/02	0816	2245.47	2.98		K	JW
			06/07/02	0744	2268.95	2.93		K	JW
059	WRS-C-7	MM-3	06/06/02	0836	3371.64	2.99		K	JW
			06/07/02	0800	3395.06	2.99		K	JW
060	HUS-C-7	MB-3	06/06/02	0901	3051.67	2.99		K	JW
			06/07/02	0826	3075.01	2.98		K	JW
061	FRS-C-8	MH-3	06/10/02	0704	3117.58	2.98		K	AC
			06/11/02	0625	3140.92	2.98		K	AC
062	FRS-C-8-FS	MG-3	06/10/02	0704	3117.58	2.98		K	AC
			06/11/02	0625	3140.92	2.99		K	AC
063	HES-C-8	MD-3	06/10/02	0756	3132.68	2.98		K	AC
			06/11/02	0714	3155.99	2.90		K	AC
064	CES-C-8	MJ-3	06/10/02	0828	12680.66	2.98		K	AC
			06/11/02	0753	12704.08	2.92		K	AC
065	WES-C-8	MK-3	06/10/02	0856	2268.95	2.98		K	AC
			06/11/02	0827	2292.46	2.98		K	AC
066	WRS-C-8	MM-3	06/10/02	0914	3395.06	2.98		K	AC
			06/11/02	0849	3418.64	2.98		K	AC
067	HUS-C-8	MB-3	06/10/02	0937	3075.10	2.98		K	AC
			06/11/02	0926	3098.92	2.94		K	AC
068	FRS-C-8-TS	N/A	06/10/02	1154	N/A	N/A		K	AC
			N/A	N/A	N/A	N/A		N/A	N/A
069	FRS-C-8-TB	N/A	06/10/02	1154	N/A	N/A		K	AC
			N/A	N/A	N/A	N/A		N/A	N/A
070	FRS-C-9	MH-3	06/11/02	0628	3140.97	2.98		K	AC
			06/12/02	0623	3164.87	2.96		K	AC
071	FRS-C-9-C	MG-3	06/11/02	0628	3140.97	2.98		K	AC
			06/12/02	0623	3164.87	2.98		K	AC
072	HES-C-9	MD-3	06/11/02	0717	3156.06	2.98		K	AC
			06/12/02	0713	3179.99	3.00		K	AC

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
073	HES-C-9-C	ME-3	06/11/02	0717	3156.06	2.98		K	AC
			06/12/02	0713	3179.99	3.10		K	AC
074	CES-C-9	MJ-3	06/11/02	0755	12704.11	2.98		K	AC
			06/12/02	0751	12728.05	2.93		K	AC
075	CES-C-9-C	MI-3	06/11/02	0755	12704.11	2.98		K	AC
			06/12/02	0751	12728.05	3.07		K	AC
076	WES-C-9	MK-3	06/11/02	0829	2292.50	2.98	Clean up in progress around area.	K	AC
			06/12/02	0825	2316.43	2.88		K	AC
077	WES-C-9-C	MF-3	06/11/02	0829	2292.50	2.98	Clean up in progress around area.	K	AC
			06/12/02	0825	2316.43	3.00		K	AC
078	WRS-C-9	MM-3	06/11/02	0851	3418.68	2.98		K	AC
			06/12/02	0844	3442.55	2.98		K	AC
079	WRS-C-9-C	MT-3	06/11/02	0851	3418.68	2.98		K	AC
			06/12/02	0844	3442.55	2.98		K	AC
080	HUS-C-9	MB-3	06/11/02	0929	3098.96	2.98		K	AC
			06/12/02	0912	3122.68	2.95		K	AC
081	HUS-C-9-C	MU-3	06/11/02	0929	3098.96	2.98		K	AC
			06/12/02	0912	3122.68	2.92		K	AC
082	FRS-C-10	MH-3	06/12/02	0625	3164.91	2.98		K	AC
			06/13/02	0557	3188.46	2.96		K	AC
083	HES-C-10	MD-3	06/12/02	0717	3180.04	2.98		K	AC
			06/13/02	0648	3203.56	3.00		K	AC
084	CES-C-10	MJ-3	06/12/02	0755	12728.11	2.98		K	AC
			06/13/02	0727	12751.65	2.75		K	AC
085	WES-C-10	MK-3	06/12/02	0828	2316.47	2.98		K	AC
			06/13/02	0759	2339.99	2.98		K	AC
086	WRS-C-1O	MM-3	06/12/02	0847	3442.60	2.98		K	AC
			06/13/02	0816	3466.10	3.00		K	AC
087	HUS-C-10	MB-3	06/12/02	0915	3122.72	2.98		K	AC
			06/13/02	0842	3146.17	3.00		K	AC
088	FRS-C-11	MH-3	06/13/02	0559	3188.48	2.98		K	AC
			06/14/02	0553	3212.38	2.98		K	AC
089	HES-C-11	MD-3	06/13/02	0650	3203.58	2.98		K	AC
			06/14/02	0638	3227.39	2.92		K	AC
090	CES-C-11	MJ-3	06/13/02	0730	12751.69	2.98	LOW FLOW	K	AC
			06/14/02	0710	12775.36	1.94		K	AC

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
091	WES-C-11	MK-3	06/13/02	0801	2340.03	2.98		K	AC
			06/14/02	0740	2363.67	3.04		K	AC
092	WRS-C-11	MM-3	06/13/02	0818	3466.13	2.98		K	AC
			06/14/02	0756	3489.75	2.97		K	AC
093	HUS-C-11	MB-3	06/13/02	0843	3146.19	2.98		K	AC
			06/14/02	0818	3169.80	3.06		K	AC
094	FRS-C-12	MH-3	06/17/02	0658	3212.40	2.98		K	JW
			06/18/02	0645	3236.18	2.93		K	JW
095	FRS-C-12-FS	MG-3	06/17/02	0658	3212.40	2.98		K	JW
			06/18/02	0645	3236.18	2.98		K	JW
096	HES-C-12	MD-3	06/17/02	0748	3227.42	2.98		K	JW
			06/18/02	0739	3251.26	2.97		K	JW
097	CES-C-12	MJ-3	06/17/02	0823	12775.42	2.98	CHANGED FITTING (LEAK)	K	JW
			06/18/02	0820	12799.38	2.97		K	JW
098	WES-C-12	MK-3	06/17/02	0902	2363.71	2.98		K	JW
			06/18/02	0859	2387.66	2.97		K	JW
099	WRS-C-12	MM-3	06/17/02	0921	3489.77	2.98		K	JW
			06/18/02	0925	3513.85	2.95		K	JW
100	HUS-C-12	MB-3	06/17/02	0952	3169.80	2.98		K	JW
			06/18/02	0959	3193.94	2.95		K	JW
101	FRS-C-12-TS	N/A	06/17/02	1005	N/A	N/A		K	JW
			N/A	N/A	N/A	N/A		N/A	N/A
102	FRS-C-12-TB	N/A	06/17/02	1005	N/A	N/A		K	JW
			N/A	N/A	N/A	N/A		N/A	N/A
103	FRS-C-13	MH-3	06/18/02	0649	3236.25	2.99		K	JW
			06/19/02	0631	3259.95	2.96		K	JW
104	FRS-C-13C	MG-3	06/18/02	0649	3236.25	2.98		K	JW
			06/19/02	0631	3259.95	2.97		K	JW
105	HES-C-13	MD-3	06/18/02	0742	3251.32	2.98		K	JW
			06/19/02	0729	3275.09	2.97		K	JW
106	HES-C-13C	ME-3	06/18/02	0742	3251.32	2.98		K	JW
			06/19/02	0729	3275.09	2.96		K	JW
107	CES-C-13	MJ-3	06/18/02	0824	12799.45	2.98		K	JW
			06/19/02	0811	12823.23	3.08		K	JW
108	CES-C-13C	MI-3	06/18/02	0824	12799.45	2.98		K	JW
			06/19/02	0811	12823.23	2.96		K	JW

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CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
109	WES-C-13	MK-3	06/18/02	0903	2387.74	2.98		K	JW
			06/19/02	0848	2411.47	2.98		K	JW
110	WES-C-13C	MF-3	06/18/02	0903	2387.74	2.98		K	JW
			06/19/02	0848	2411.47	2.97		K	JW
111	WRS-C-13	MM-3	06/18/02	0929	3513.91	2.98		K	JW
			06/19/02	0919	3537.74	2.98		K	JW
112	WRS-C-13C	MT-3	06/18/02	0929	3513.91	2.98		K	JW
			06/19/02	0919	3537.74	2.97		K	JW
113	HUS-C-13	MB-3	06/18/02	1002	3193.98	2.98		K	JW
			06/19/02	0948	3217.74	2.99		K	JW
114	HUS-C-13C	MU-3	06/18/02	1002	3193.98	2.97		K	JW
			06/19/02	0948	3217.74	2.96		K	JW
115	FRS-C-14	MH-3	06/19/02	0635	3260.02	2.98		K	JW
			06/20/02	0616	3283.70	3.00		K	JW
116	HES-C-14	MD-3	06/19/02	0733	3275.17	2.98		K	JW
			06/20/02	0706	3298.71	2.99		K	JW
117	CES-C-14	MJ-3	06/19/02	0816	12823.31	2.98		K	JW
			06/20/02	0741	12846.73	3.00		K	JW
118	WES-C-14	MK-3	06/19/02	0854	2411.57	2.99		K	JW
			06/20/02	0814	2434.91	3.00		K	JW
119	WRS-C-14	MM-3	06/19/02	0923	3537.81	2.97		K	JW
			06/20/02	0836	3561.02	2.96		K	JW
120	HUS-C-14	MB-3	06/19/02	0953	3217.83	2.98		K	JW
			06/20/02	0903	3240.99	2.96		K	JW
121	FRS-C-15	MH-3	06/20/02	0620	3283.76	2.99		K	JW
			06/21/02	0601	3307.45	2.98		K	JW
122	HES-C-15	MD-3	06/20/02	0708	3298.75	2.98		K	JW
			06/21/02	0646	3322.38	2.97		K	JW
123	CES-C-15	MJ-3	06/20/02	0742	12846.75	2.98		K	JW
			06/21/02	0718	12870.35	3.08		K	JW
124	WES-C-15	MK-3	06/20/02	0815	2434.92	2.98		K	JW
			06/21/02	0750	2458.53	3.06		K	JW
125	WRS-C-15	MM-3	06/20/02	0838	3561.05	2.98		K	JW
			06/21/02	0808	3584.55	3.00		K	JW
126	HUS-C-15	MB-3	06/20/02	0904	3241.01	2.98		K	JW
			06/21/02	0844	3264.67	3.00		K	JW

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CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

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Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
127	FRS-C-16	MH-3	06/24/02	0650	3307.45	2.98		K	AC
			06/25/02	0622	3330.97	3.00		K	AC
128	FRS-C-16-FS	MG-3	06/24/02	0650	3307.45	2.98		K	AC
			06/25/02	0622	3330.97	2.90		K	AC
129	HES-C-16	MD-3	06/24/02	0741	3322.39	2.98		K	AC
			06/25/02	0713	3345.93	2.92		K	AC
130	CES-C-16	MJ-3	06/24/02	0816	12870.36	2.98		K	AC
			06/25/02	0753	12893.98	2.97		K	AC
131	WES-C-16	MK-3	06/24/02	0844	2458.54	2.98		K	AC
			06/25/02	0827	2482.25	2.95		K	AC
132	WRS-C-16	MM-3	06/24/02	0901	3584.56	2.98		K	AC
			06/25/02	0850	3608.36	2.98		K	AC
133	HUS-C-16	MB-3	06/24/02	0919	3337.27	2.98		K	AC
			06/25/02	0916	3361.22	2.98		K	AC
134	FRS-C-16-TS	N/A	06/24/02	1500	N/A	N/A		K	AC
			N/A	N/A	N/A	N/A		N/A	N/A
135	FRS-C-16-TB	N/A	06/24/02	1501	N/A	N/A		K	AC
			N/A	N/A	N/A	N/A		N/A	N/A
136	FRS-C-17	MH-3	06/25/02	0625	3331.02	2.98		K	AC
			06/26/02	0557	3354.56	2.98		k	AC
137	FRS-C-17-C	MG-3	06/25/02	0625	3331.02	2.98		K	AC
			06/26/02	0557	3354.56	2.99		K	AC
138	HES-C-17	MD-3	06/25/02	0716	3345.98	2.98		K	AC
			06/26/02	0656	3369.65	2.98		K	AC
139	HES-C-17-C	ME-3	06/25/02	0716	3345.98	2.98		K	AC
			06/26/02	0656	3369.65	3.00		K	AC
140	CES-C-17	MJ-3	06/25/02	0756	12894.02	2.98		K	AC
			06/26/02	0734	12917.67	3.00		K	AC
141	CES-C-17-C	MI-3	06/25/02	0756	12894.02	2.98		K	AC
			06/26/02	0734	12917.67	2.97		K	AC
142	WES-C-17	MK-3	06/25/02	0829	2482.28	2.98	NO POWER, TRIPPED CKT BKR	K	AC
			06/26/02	0824	2482.66	0.00		K	AC
143	WES-C-17-C	MF-3	06/25/02	0829	2482.28	2.98	NO POWER, TRIPPED CKT BKR	K	AC
			06/26/02	0824	2482.66	0.00		K	AC
144	WRS-C-17	MM-3	06/25/02	0853	3608.41	2.98		K	AC
			06/26/02	0846	3632.30	2.99		K	AC

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CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
145	WRS-C-17-C	MT-3	06/25/02	0853	3608.41	2.98		K	AC
			06/26/02	0846	3632.30	2.93		K	AC
146	HUS-C-17	MB-3	06/25/02	0917	3361.24	2.98		K	AC
			06/26/02	0910	3385.13	2.98		K	AC
147	HUS-C-17-C	MU-3	06/25/02	0917	3361.24	2.98		K	AC
			06/26/02	0910	3385.13	2.94		K	AC
148	FRS-C-18	MH-3	06/26/02	0559	3354.59	2.98		K	AC
			06/27/02	0547	3378.39	2.98		K	AC
149	HES-C-18	MD-3	06/26/02	0658	3369.68	2.98		K	AC
			06/27/02	0641	3393.39	2.98		K	AC
150	CES-C-18	MJ-3	06/26/02	0736	12917.71	2.98		K	AC
			06/27/02	0716	12941.36	3.00		K	AC
151	WES-C-18	MK-3	06/26/02	0827	2482.80	2.98		K	AC
			06/27/02	0747	2506.11	3.05		K	AC
152	WES-C-18-C	MF-3	06/26/02	0827	2482.80	2.98	MAKE UP COLOCATED RUN	K	AC
			06/27/02	0747	2506.11	3.00		K	AC
153	WRS-C-18	MM-3	06/26/02	0848	3632.33	2.98		K	AC
			06/27/02	0807	3655.66	3.00		K	AC
154	HUR-C-18	MB-3	06/26/02	0913	3385.17	2.98		K	AC
			06/27/02	0829	3408.43	3.00		K	AC
155	FRS-C-19	MH-3	06/27/02	0548	3378.40	2.98		K	AC
			06/28/02	0524	3402.00	2.95		K	AC
156	HES-C-19	MD-3	06/27/02	0642	3393.42	2.98		K	AC
			06/28/02	0612	3416.92	2.91		K	AC
157	CES-C-19	MJ-3	06/27/02	0717	12941.37	2.98		K	AC
			06/28/02	0651	12964.94	2.88		K	AC
158	WES-C-19	MK-3	06/27/02	0749	2506.14	2.98		K	AC
			06/28/02	0718	2529.64	2.93		K	AC
159	WRS-C-19	MM-3	06/27/02	0809	3655.68	2.98		K	AC
			06/28/02	0736	3679.13	2.98		K	AC
160	HUR-C-19	MB-3	06/27/02	0830	3408.45	2.98		K	AC
			06/28/02	0756	3431.88	2.93		K	AC
161	FRS-C-20	MH-3	07/01/02	0701	3402.04	2.98		K	JW
			07/02/02	0635	3425.60	2.99		K	JW
162	FRS-C-20-FS	MG-3	07/01/02	0701	3402.04	2.98		K	JW
			07/02/02	0635	3425.60	3.00		K	JW

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CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

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Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
163	FRS-C-20-TS	N/A	07/01/02	0705	N/A	N/A		K	JW
			N/A	N/A	N/A	N/A		N/A	N/A
164	FRS-C-20-TB	N/A	07/01/02	0706	N/A	N/A		K	JW
			N/A	N/A	N/A	N/A		N/A	N/A
165	HES-C-20	MD-3	07/01/02	0802	3416.94	2.98		K	JW
			07/02/02	0727	3440.36	3.00		K	JW
166	CES-C-20	MJ-3	07/01/02	0835	12964.98	2.98		K	JW
			07/02/02	0808	12988.52	2.98		K	JW
167	WES-C-20	MK-3	07/01/02	0906	2529.66	2.98		K	JW
			07/02/02	0843	2553.27	2.98		K	JW
168	WRS-C-20	MM-3	07/01/02	0921	3679.16	2.98		K	JW
			07/02/02	0905	3702.89	2.98		K	JW
169	HUR-C-20	MB-3	07/01/02	0942	3499.40	2.98		K	JW
			07/02/02	0934	3522.78	2.99		K	JW
170	FRS-C-21	MH-3	07/02/02	0639	3425.67	2.98		K	JW
			07/03/02	0548	3448.82	2.98		K	JW
171	FRS-C-21-C	MG-3	07/02/02	0639	3425.67	2.98		K	JW
			07/03/02	0548	3448.82	3.00		K	JW
172	HES-C-21	MD-3	07/02/02	0730	3440.41	2.98		K	JW
			07/03/02	0640	3463.57	2.97		K	JW
173	HES-C-21-C	ME-3	07/02/02	0730	3440.41	2.98		K	JW
			07/03/02	0640	3463.57	3.03		K	JW
174	CES-C-21	MJ-3	07/02/02	0811	12988.57	2.98		K	JW
			07/03/02	0722	13011.76	2.97		K	JW
175	CES-C-21-C	MI-3	07/02/02	0811	12988.57	2.98		K	JW
			07/03/02	0722	13011.76	3.01		K	JW
176	WES-C-21	MK-3	07/02/02	0846	2553.32	2.98		K	JW
			07/03/02	0800	2576.55	3.05		K	JW
177	WES-C-21-C	MF-3	07/02/02	0846	2553.32	2.98		K	JW
			07/03/02	0800	2576.55	3.00		K	JW
178	WRS-C-21	MM-3	07/02/02	0909	3702.95	2.98		K	JW
			07/03/02	0846	3726.57	2.97		K	JW
179	WRS-C-21-C	MT-3	07/02/02	0909	3702.95	2.98		K	JW
			07/03/02	0846	3726.57	2.98		K	JW
180	HUR-C-21	MB-3	07/02/02	0937	3522.83	2.98	POWER OUTAGE	K	JW
			07/03/02	0922	3526.25	2.99		K	JW

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CARTRIDGE FIELD LOG SHEET

Project: Chlorothalonil Ambient Air Monitoring in Fresno County

Project #: P-02-002 On Flow: 3.00 ±0.02lpm Off Flow: 3.00 lpm ±10%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	Comments	Weather K,P,C,F&R On / Off	Initials On / Off
181	HUR-C-21-C	MU-3	07/02/02	0937	3522.83	2.98	POWER OUTAGE	K	JW
			07/03/02	0922	3526.25	3.00		K	JW

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Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)